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The importance of spin-orbit coupling and electron correlation in the rationalization of the ground state of the CUO molecule

Ivan Infante and Lucas Visscher

Section Theoretical Chemistry, Faculty of Sciences, Vrije Universiteit Amsterdam, De Boelelaan 1083, 1081 HV Amsterdam, The Netherlands

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We present calculations at the relativistic coupled cluster theory that predict the $^1\Sigma_0^+$ ground state of CUO to lie 58.2 kJ/mol below the first excited state, $^3\Phi_2$. This can be contrasted with the outcome of earlier density functional theory and complete active space second order perturbation theory (CASPT2) calculations that both predicted a $^3\Phi_2$ ground state upon inclusion of spin-orbit coupling in the calculations. Our result gives further justification to the interpretation of the measured frequency shifts of this species in various noble gas matrices as being caused by significant interaction between the uranium and the heavier noble gas atoms. © 2004 American Institute of Physics. [DOI: 10.1063/1.1784778]

I. INTRODUCTION

Many new small actinide molecules have been synthesized and characterized in recent years via laser ablation matrix infrared experiments.^{1,2} Of the new species the small CUO molecule has attracted much attention due to its remarkable behavior in different rare gas matrices.^{3,4} Bringing laser ablated uranium atoms in contact with CO, the strong triple bond of the carbon monoxide is broken leaving CUO as the primary product of a reaction that also gives other secondary components like OUCCO.⁵ Upon trapping the CUO molecule in different solid noble-gas (Ng) matrices Andrews and co-workers^{6,7} found a large vibration frequency shift that could be explained by assuming that the ground state of the molecule is changed due to the interaction with the noble gas matrix: in neon the interaction is weak and the same singlet ground state is found as in the gas phase, whereas the stronger interaction with argon or krypton is sufficient to make the lowest lying triplet state the ground state. Since the two states differ by occupation of either a bonding (in case of the singlet) or of a nonbonding uranium *f*-orbital (in case of the triplet states) a large frequency shift in the C-U stretching vibration is observed.

The simple intuitive picture sketched above was initially supported by density functional theory (DFT) calculations of Bursten *et al.*⁸ which indicated that the interaction with a single argon atom is already enough to overcome the energy difference of only a few kJ/mol between the $^1\Sigma^+$ and the $^3\Phi$ states. They furthermore showed that the experimental infrared spectra of CUO in CUO-Ne and in CUO-Ar matrices match precisely the vibrational frequencies computed by DFT theory for the gas phase species. Experimentally, the normal modes have frequencies of 1047.3 and 872.2 cm⁻¹ (CUO-Ne matrix) and 852.5 and 804.3 cm⁻¹ (CUO-Ar), while the theoretical frequencies are 1049 and 874 cm⁻¹ ($^1\Sigma^+$) and 943 and 902 cm⁻¹ ($^3\Phi$), respectively. The DFT calculations of Bursten were, however, done without considering spin-orbit coupling (SOC) effects that can easily overcome such small energy differences between singlet and triplet states. Roos, Widmark, and Gagliardi⁹ performed accurate

CASPT2 calculations and found that already without including SOC the triplet state is the lowest in the gas phase. With SOC the triplet state is found to lie about 50 kJ/mol below the singlet. This is in contradiction with the later experiments of Andrews and co-workers which indicate that more than one rare gas atom is bound to the CUO.⁶ With more interacting Ng atoms the energy difference between the singlet and triplet (with the singlet being lower) should be larger in order to prevent that also the weak interaction with neon would change the ground state. Both sides agree that the experimental evidence for an inversion of ground state relative to the gas phase or weakly bound Ne atoms is overwhelming, but the question remains how this trend can be reproduced in a theoretical description.

In this work we intend to look at the effect of SOC in a DFT approach and to check how much the choice of functional influences the computed energy difference. To give an independent verification of the *ab initio* results we have performed calculations with the Dirac-Coulomb coupled cluster with single and double excitations with perturbative treatment of triples [DC-CCSD(T)] method¹⁰ to allow for a very precise treatment of both relativistic and electron correlation effects. Also in this method it is possible to isolate SOC effects from other relativistic effects, which makes the analysis of results easier. With the two schemes we can study all four aspects of the stabilization of one state over the other: the difference in bond lengths, the relativistic approximation, the SOC correction, and the correlation energy. Since several multiplet states arise from the low-lying unoccupied *f* orbitals from the uranium, the use of single reference method like DC-CCSD(T) or DFT may not be appropriate. We therefore also performed a number of calculations using the multireference (Fock space¹¹) CCSD approaches to verify the consistency of the computed results. We will divide the discussion of the different theoretical results that we achieved into three parts. First, we vary the structure (bond lengths) and see how this affects the energies of the two states of interest. We then approximate the Hamiltonian to get information about the SOC effect; and finally we compare how the dif-

ferent methods (DFT, CCSD, MR-CCSD, CASPT2 treat the correlation energy. Furthermore, other contributions that are analyzed in more detail are the choice of the basis sets (for all methods), the exchange-correlation (xc) functional (for DFT), and the active space (for CC and MR-CC).

Before continuing, we remember that in the presence of a spin-orbit (SO) term, the $^3\Phi$ state is decomposed in three different states labeled by the Ω value (with Ω the projection of the total electronic angular momentum on the molecular axis). The $^3\Phi_2$ and $^3\Phi_4$ states may be described by the single determinant wave functions $|\sigma_{-1/2}\phi_{5/2}|$ and $|\sigma_{1/2}\phi_{7/2}|$, respectively; but $^3\Phi_3$ interacts with $^1\Phi_3$ and needs to be described by a two-determinant reference functions including both $|\sigma_{-1/2}\phi_{7/2}|$ and $|\sigma_{1/2}\phi_{5/2}|$. This state is less accessible for CC and DFT approaches, and we therefore chose to focus only on the lowest $^3\Phi_2$ component. In conventional approaches, in which SOC is considered as a perturbation, one also finds a significant mixing of this state with the $^3\Delta_2$ state due to the occurrence of SOC matrix elements between the almost degenerate $\phi_{5/2}$ and $\delta_{5/2}$ orbitals. This mixing need not be considered in variational SOC calculations—because these matrix elements are close to zero according to Brillouins theorem—which makes the single reference CC approach possible.

To shorten the notation we define ΔE_Ω as the energy gap between the components of the triplet state $^3\Phi_\Omega$ (with $\Omega=2, 3, 4$) and the singlet $^1\Sigma_0^+$. In spin-free calculations we will simply use the notation ΔE .

II. COMPUTATIONAL DETAILS

All-electron DFT calculations were done using the scalar and spin-orbit zeroth order regular approximation (ZORA) Refs. 12–15 as implemented in the ADF2003 package.¹⁶ ADF offers a wide choice of functionals that will be indicated by the acronym used in the program. The primary reference can easily be found in the documentation of the program and will not be listed unless explicitly discussed in the text. The all-electron CCSD(T) calculations were done using the full four-component Dirac-Coulomb (DC) Hamiltonian, as implemented in the DIRAC program.¹⁷ For purpose of analysis we have also made use of the transformed DC equation,¹⁸ which can be approximated to the scalar relativistic spin-free (SFDC) Hamiltonian.¹⁹ For computational efficiency only the (LL|LL) and (SS|LL) two-electron integrals (L=large; S=small) were included. Test calculations that included the more numerous but numerically insignificant (SS|SS) integrals showed that associated error is marginal, only 0.4% in ΔE_Ω .

Geometry optimizations have been performed at ZORA/DFT level applying a convergence on the gradient at 10^{-4} with accuracy on the integration grid of 10^{-10} . In these ZORA/DFT calculations we used a triple- ζ basis augmented by two polarization (TZ2P) functions on all the atoms. The $1s$ core of C and O atoms and all orbitals up to the $5d$ shell for U have been kept frozen based on relativistic atomic calculations. Single point *ab initio* calculations were carried out using fully uncontracted basis sets taking the exponents from the cc-pVTZ Refs. 20–22 sets for the carbon and oxy-

gen atoms, and either the $26s21p17d12f$ basis set of de Jong²³ or the $33s29p21d15f3g1h$ basis set of Faegri.²⁴

The computed correlation energy in CCSD(T) will depend on the choice of the active space. The important orbitals for the C and O atoms are the subvalence $2s$ and the valence $2p$ orbitals. Correlation of the core $1s$ electrons may be considered unimportant at the level of accuracy that we try to achieve. For uranium the situation is more complicated and different partitionings of the valence shell are possible. The minimal choice for an active space is to consider only the six electrons in the $5f$, $6d$, and $7s$ orbitals. This gives a total minimum number of electrons to be correlated of 12. Taking also the subvalence uranium $6p$ and carbon and oxygen $2s$ electrons into consideration increases this number to 22 electrons. Core-valence correlations due to interaction with the deeper lying $5d$ and $6s$ electrons may also be important and are treated with the largest active space used in this work: 34 electrons. Besides choosing the number of electrons to be correlated we also restricted the full set of virtual orbitals to the set relevant for valence and subvalence correlation. We did so by deleting virtuals with an orbital energy above 10 a.u.

III. RESULTS AND DISCUSSIONS

A. Geometry

The $^1\Sigma_0^+$ and $^3\Phi_2$ states have a rather different C-U bond length since one electron less contributes to C-U bonding in the triplet state. This gives an elongation of about 0.10 Å of the C-U bond and 0.02 Å of the U-C bond in the triplet state. To avoid large errors in the computation of the relative energies it is, therefore, important to compute the adiabatic energy differences rather than employing a common geometry. This point was already mentioned by Roos, Widmark, and Gagliardi⁹ and is confirmed by our DC-CCSD(T) calculations. For example, at the DC-CCSD(T) level of theory, we compute $\Delta E_2=15.1$ kJ/mol using the $^1\Sigma_0^+$ geometry and $\Delta E_2=40.6$ kJ/mol, with two separate geometries. Since DC-CCSD(T) calculations are computational intensive, full geometry optimizations were not feasible at this level of theory. We therefore had to choose geometries optimized at a different level of theory. The question then arises whether it is better to use either the effective core potentials ECP-CASPT2 or Douglas-Kroll-Hess DKH-CASPT2 structures reported by Roos, Widmark, and Gagliardi or to use the ZORA-DFT structures. The ECP-CASPT2 geometries differ most from the DFT ones so that a comparison of the difference between the two structures serves to give some indication about the sensitivity of the computed ΔE_2 to the optimization procedure. As shown in Table I, all bond distances optimized at ECP-CASPT2 level are slightly larger (about 0.01–0.03 Å) than those optimized with ZORA-DFT, with as exception the C-U bond in the singlet state that is nearly identical in the two methods. Table I shows that there is some influence of the choice of structure, about 8 kJ/mol on the ΔE_2 , but this difference is small enough to not affect the conclusions drawn in this work. For the DC-CCSD core-correlation calculations reported below we used the ECP-CASPT2 geometries.

TABLE I. Adiabatic $\Delta E_2 = E(^3\Phi_2) - E(^1\Sigma_0^+)$ energies (kJ/mol) computed at different level of theory. The geometries labeled DFT are obtained by optimization of $^1\Sigma_0$ and $^3\Phi_2$ states at DFT/BPW91 level; the ECP-CASPT2 geometries are taken from Ref. 9.

Hamiltonian method	ZORA DFT/BPW91	DC HF	DC CCSD	DC CCSD(T)	DC MRCCSD
ΔE_2 //DFT ^a	-2.9	-24.7	46.4	52.7	
ΔE_2 //CASPT2 ^b	2.5	-36.8	34.3	40.6	34.3

^aThe bond lengths in the singlet geometry: C-U 1.808 Å and C-U 1.760 Å; The bond lengths in the triplet geometry: C-U 1.833 Å and C-U 1.865 Å.

^bThe bond lengths in the singlet geometry: C-U 1.808 Å and C-U 1.772 Å; The bond lengths in the triplet geometry: C-U 1.842 Å and C-U 1.889 Å.

B. Spin-orbit coupling

In order to study the effect of SOC we first need to look closer at the electronic configuration of the CUO molecule. In Table II we list the DFT orbital energies obtained at DFT/BPW91 Ref. 25 and DFT/BPW91+SO level of theory for the singlet state. The orbital energy difference between a virtual orbital and the highest occupied molecular orbital (HOMO) gives a first indication of the excitation energy.²⁶ We find a non-Aufbau configuration with the ϕ LUMO (LUMO—lowest unoccupied molecular orbital) lying lower than the HOMO. This does indicate the near degeneracy of the singlet and triplet states. Apart from the ϕ LUMO we find a δ orbital at low energy that is also largely a uranium $5f$ -orbital, but with some $6d$ character. The antibonding σ and π orbitals lie at higher energy. Due to SOC all but the σ orbital energies are split into two levels and we find that the splitting between the $\phi_{5/2}$ and $\phi_{7/2}$ is large enough to influence the order of states.

We first performed DFT calculations similar to the work of Bursten *et al.*,^{5,8,27} to see whether use of the more accurate relativistic approximation, ZORA, instead of the quasirelativistic Pauli approach would make any difference. This is not the case: the scalar results shown in Table II are consistent with the ones obtained by Andrews, giving a higher stabilization of the $^1\Sigma_0^+$ states over the $^3\Phi$ state of $\Delta E = 12.6$ kJ/mol. The $^3\Delta$ state formed by occupying the δ orbital lies also close in energy ($\Delta E = 40.6$ kJ/mol) while the other states ($^3\Sigma$ and $^3\Pi$) lie at much higher in energy, as expected. SOC is now considered by computing the energy of the lowest Ω states of a given multiplet. Since ADF cannot optimize structures when the SOC option is activated, we performed single point runs on the geometries obtained at the spin-free level assuming the SOC-induced structural effects are small. We see that SOC indeed has a significant effect on the relative energies ranging from -1.5 kJ/mol for the $^3\Delta$ state to -15.5 kJ/mol for ΔE_2 . The latter shift brings the $^3\Phi_2$ state below the $^1\Sigma_0^+$ state ($\Delta E_2 = -2.9$ kJ/mol), which is in contradiction to the picture sketched to explain the experimental findings.

Given this failure of the DFT approach to confirm the experimental picture we now examine the CUO molecule using *ab initio* methods. At the SFDC-HF level of theory (four component Hamiltonian, excluding SOC) we find $^1\Sigma^+$ and $^3\Phi$ at approximately the same energy with $\Delta E = 2.9$ kJ/mol. With SOC the $^3\Phi_2$ state falls below the $^1\Sigma_0^+$

TABLE II. Composition and orbital energy eigenvalue of orbitals computed at the scalar and SOC ZORA-DFT level of theory. Only the most important contributions are listed.

	Symmetry	Composition (SF)		Energy (SF)	Energy (SO)
		(%)	Type		
LUMO+6	$\pi_{3/2}$	43 24 11 11	$5f_{z2y}(\text{U})$ $7p_y(\text{U})$ $2p_y(\text{C})$ $2p_y(\text{O})$	-127.4	-107.1
LUMO+5	$\pi_{1/2}$	43 24 11 11	$5f_{z2x}(\text{U})$ $7p_x(\text{U})$ $2p_x(\text{C})$ $2p_x(\text{O})$	-127.4	-145.7
LUMO+4	$\sigma_{1/2}$	55 14 12 6	$7s(\text{U})$ $2p_z(\text{C})$ $6d_{z2}(\text{U})$ $2p_z(\text{O})$	-297.2	-298.2
LUMO+3	$\delta_{5/2}$	91 9	$5f_{xyz}(\text{U})$ $6d_{xy}(\text{U})$	-349.3	-321.3
LUMO+2	$\delta_{3/2}$	91 9	$5f_z(\text{U})$ $6d_{x2-y2}(\text{U})$	-349.3	-365.7
LUMO+1	$\phi_{7/2}$	100	$5f_y(\text{U})$	-417.8	-384.0
LUMO	$\phi_{5/2}$	100	$5f_x(\text{U})$	-417.8	-446.7
HOMO	$\sigma_{1/2}$	39 24 15 9	$5f_{z3}(\text{U})$ $2p_z(\text{C})$ $7s(\text{U})$ $6d_{z2}(\text{U})$	-398.5	-396.6
HOMO-1	$\pi_{3/2}$	44 34 21	$2p_y(\text{C})$ $5f_{z2y}(\text{U})$ $6d_{yz}(\text{U})$	-482.5	-479.6
HOMO-2	$\pi_{1/2}$	44 34 21	$2p_x(\text{C})$ $5f_{z2x}(\text{U})$ $6d_{xz}(\text{U})$	-482.5	-492.1
HOMO-3	$\sigma_{1/2}$	32 26 23 8	$2p_z(\text{O})$ $5f_{z3}(\text{U})$ $2s(\text{C})$ $6p_z(\text{U})$	-710.2	-709.2
HOMO-4	$\pi_{3/2}$	78 11 9	$2p_y(\text{O})$ $6d_{yz}(\text{U})$ $5f_{z2y}(\text{U})$	-883.8	-877.1
HOMO-5	$\pi_{1/2}$	78 11 9	$2p_x(\text{O})$ $6d_{xz}(\text{U})$ $5f_{z2x}(\text{U})$	-883.8	-890.6
HOMO-6	$\sigma_{1/2}$	43 35 11	$2s(\text{C})$ $2p_z(\text{O})$ $5d_{z2}(\text{U})$	-979.4	-980.3

state with $\Delta E_2 = -36.8$ kJ/mol. From analysis of the orbitals from the SOC calculations we furthermore deduce that the $\phi_{5/2}$ orbital acquires 10% $\delta_{5/2}$ character, which is in reasonable agreement with the 14% admixture of $^3\Delta_2$ state in the $^3\Phi_2$ state found in the multistate CASPT2 calculations by Roos, Widmark, and Gagliardi.⁹

The splitting between the $^1\Sigma_0^+$ and $^3\Phi$ states is larger than the -15.5 kJ/mol found at DFT level but both methods give the same qualitative picture. Inclusion of electron cor-

TABLE III. Comparison of computed energy difference (kJ/mol) relative to the $^1\Sigma_0^+$ energy for various GGA xc functionals Refs. 28–32. In the SOC case we have chosen the triplet states with lowest value of Ω as indicated. For the meta-GGA functional HCTH/402 only the SF value can be computed.

	BPW91 $^3\Sigma_0^+$	BPW91 $^3\Pi_0$	BPW91 $^3\Delta_1$	BPW91 $^3\Phi_2$	BLYP $^3\Phi_2$	PBE $^3\Phi_2$	RPBE $^3\Phi_2$	revPBE $^3\Phi_2$	HCTH/402 $^3\Phi_2$
SF	81.6	236.4	40.6	12.6	13.8	12.6	6.3	5.4	2.5
SOC	77.8	226.8	38.9	−2.9	−2.2	−2.4	−8.5	−9.2	...

relation effects is thus required to reach agreement with the experimental findings. We chose to use the DC-CCSD(T) approach, correlating initially 22 electrons and fixing the virtual orbital threshold at 10 a.u. At SFDC-CCSD(T) level of theory correlation lowers $^1\Sigma^+$ state relative to the $^3\Phi$ state giving $\Delta E = 79.9$ kJ/mol SOC again stabilizes the $^3\Phi_2$ state but due to the larger initial difference the computed energy difference ΔE_2 remains positive at 40.6 kJ/mol. The SOC splitting of 39.3 kJ/mol itself is almost identical to the 39.7 kJ/mol found in absence of correlation (Table IV). This tells us that the main difference between DFT and *ab initio* approach lies in the description of the correlation energy. The somewhat larger SO splitting found in the *ab initio* calculation may be due to the more compact ϕ spinor determined by the Hartree-Fock (HF) procedure, but is not decisive in explaining the observed difference. Decisive is the fact that the $^1\Sigma^+$ state is more stabilized by electron correlation than the $^3\Phi$ state.

A somewhat uncertain factor in the $^3\Phi$ CCSD calculation is the fact that, for technical reasons, we needed to use noncanonical orbitals that are optimized for the average energy expression of the four determinants describing both the singlet and the triplet coupled Φ states arising from the configuration $\sigma^1\phi^1$. In order to check possible artifacts arising from this approach we also carried out calculations at MR-CCSD level. This technique, based on the Fock-space method,¹¹ allows us to compute electron affinities by adding one electron to a set of active virtual spinors. We can then compute ΔE_2 directly as the difference between the first and second electron of CUO^+ , where we take CUO^+ in its $^2\Sigma^+$ ground state that has one unpaired electron in the $\sigma_{1/2}$ spinor. Choosing as active virtuals: $\sigma_{1/2}$ and $\phi_{5/2}$, we obtain three electron affinities of CUO^+ relating to, respectively, the $^1\Sigma_0$, $^3\Phi_2$, and $^3\Phi_3$ states. The advantage of this alternative Fock-space approach lies now in the fact that a more balanced description of the singlet and the triplet states is achieved, one cannot speak of true multireference CC as symmetry prohibits mixing of the three excited states. The MR-CC results confirm the trend found in the single reference calculations giving $\Delta E_2 = 34.3$ kJ/mol.

C. Verification of the computed values

Since we are interested in a small energy gap we need to carefully examine all factors that may influence the outcome of the calculations. For the *ab initio* correlated calculations the finite size of the single particle basis set and the choice of active space are likely to be the most important sources of errors. For a DFT approach basis set truncation errors are

usually marginal but the choice of the exchange-correlation functional may be crucial. We will examine the errors in both methods in the following section.

1. DFT method

Exchange-correlation xc functionals. We already looked at the choice of the Hamiltonian and saw that the ZORA approach gives values in agreement with a Pauli Hamiltonian. To verify that the choice of functional does not influence the qualitative picture drawn from the DFT calculations we computed ΔE at SOC-free level of theory using the various xc functionals available in ADF (Table III). All modern functionals give a small energy gap that is usually positive but often somewhat smaller than with the older BPW91 functional: for example, the revPBE Refs. 28 and 29 functional gives a difference of only 6.3 kJ/mol. Adding SOC gives the same trend as seen in the BPW91 calculation: the $^3\Phi_2$ state becomes the ground state.

Basis sets and frozen cores. Another feature that might change the results is the effect of the basis set and the frozen core on uranium. All previously reported calculations were performed at TZ2P level freezing all orbitals below the uranium *5d* orbitals. To check basis set truncation and the frozen core error we also performed a calculation with a larger basis set: QZ4P and with no frozen core. This calculation gave $\Delta E = 11.3$ kJ/mol in good agreement with the $\Delta E = 10.0$ kJ/mol found in the smaller basis so we may conclude that basis set truncation errors are marginal.

2. CC and MR-CC method

Basis sets. For computational efficiency we have carried out most *ab initio* calculations using the medium sized basis set of de Jong and co-workers²³ that has no *g* or *h* functions. To check the validity of this choice, we also did calculations with the much larger Faegri set²⁴ that includes three *g* and one *h* functions.

In the computation of ΔE_2 , we found that the $^3\Phi_2$ states benefit most from the increased flexibility of the basis set. At DC-HF level, the ΔE_2 is lowered by 5.0 to −41.8 kJ/mol. At the correlated CCSD(T) level of theory we find that the energy gap ΔE_2 is decreased by 7.5 to 33.1 kJ/mol.

Given the relatively small changes due to the basis set we, however, decided to continue to work with the smaller basis set of de Jong.

Active space. Previously we indicated that it is the correlation energy that is responsible for keeping ΔE_2 positive. We now want to investigate which spinors of the uranium atom should be taken active or, in other words, to see what

TABLE IV. The computed energy differences (kJ/mol) relative to the $^1\Sigma_0^+$ energy for various *ab initio* approaches.

	DHF	CCSD				CCSD(T)			MR-CCSD			CASPT ^a
		12e	22e	34e		12e	22e	34e	12e	22e	34e	
SF	2.9		74.1				79.9		10.5
SO $\Omega=2$	-36.8	2.5	34.3	49.8	3.3	40.6	58.2	23.0	34.3	57.3		-39.7
SO $\Omega=4$	33.1	...	121.3	...		102.9	

^aReference 9.

the differential effect of core-valence correlation is. We did so by choosing three different active spaces still using a virtual orbital threshold of 10 a.u. This is in agreement with our rule of thumb that at least all virtuals that lie below minus two times the energy of the lowest occupied active orbital should be taken into account.

Table IV shows that the CCSD(T) correlation energy brings ΔE_2 from -36.8 kJ/mol at DHF level to 58.2 kJ/mol in the largest active space (34e), a total relative shift of 95.0 kJ/mol. If only the valence shell spinors (12e in the active space) of the uranium atom are taken into account a relative shift of only 40.2 kJ/mol (42% of the total shift) is computed. The subvalence U_{6s} , U_{6p} , and C_{2s} electrons contribute, thus, 37.2 kJ/mol (39%) to the relative difference in correlation energies and a nonnegligible 19% is provided by the subvalence 5d orbitals of the uranium atom. It is well known that the 6p orbitals of the uranium are chemically active and the differential effect of this core-valence correlation contribution for two states with a rather large change in C-U bond length may, therefore, not be so surprising. It is interesting to note, however, that also the correlation of the 5d orbitals is important to get quantitatively correct results. Again we also checked the outcome by comparing with MR-CCSD calculations and found that the choice of reference spinors has some effect, but does not change the qualitative picture of the importance of core-valence correlation effects. This does not solve the puzzle posed by Roos and co-workers who called the ground state of CUO a "mystery." They compared the CASSCF and CASPT2 ΔE values and found a shift of -28 kJ/mol when correlating 34 electrons, with the CASPT2 correction decreasing ΔE_2 instead of increasing it as we find in the CC calculations. This remarkable difference in the effect of dynamic correlation should be due to the difference with our approach. In our calculations all correlation effects are described at the CC level, while the CASSCF calculations already accounts for nondynamical correlation. In our calculation there is no puzzle to be solved: a ΔE_2 of 58.2 kJ/mol fits with the experimental picture in which interaction with a number of Ar atoms is required to change the ground state.

IV. CONCLUSIONS

It is difficult to produce quantitatively the small energy difference and ordering of the two lowest lying state of the CUO molecule. At SFDC-HF level of theory the two states $^1\Sigma^+$ and $^3\Phi$ are almost degenerate and we may distinguish the role of electron correlation and SOC on the relative energies of both states. Our results show that these two effects

oppose each other. Correlation tends to stabilize the more compact singlet state by almost 100 kJ/mol more than it does in the triplet state. Core-valence correlation is important and is responsible for almost half of this difference. SOC gives a consistent energy splitting of the triplet state contribution that does not depend much on the method used to compute a splitting. It lowers the lowest component, the $^3\Phi_2$ by about 40 kJ/mol. Nevertheless the effect of correlation is large enough to keep the $^1\Sigma^+$ state as ground state. At the highest level of accuracy the difference is 58.2 kJ/mol. Such an energy difference agrees well with the experimental data in which interaction with a number of heavier noble gas atoms (Ar or Kr) is required to reverse the order of the $^3\Phi_2$ and $^1\Sigma_0^+$ states.

This clear picture is not supported by other methods. Both ZORA-DFT and DKH-CASPT2 give a very small ΔE_2 that becomes negative upon inclusion of SOC. Whereas the ZORA-DFT results are difficult to analyze further it would be interesting to compare the DKH-CASPT2 approach with a similar approach based on two- or four-component orbitals that would allow for a more detailed characterization of the $^3\Phi_2$ state.

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